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ELEMENTAL FLUORINE BASED SYNTHESES OF PENTAFLUORO PHENLY AND OTHER AROMATIC PERFLUOROPOLYETHER POLYMERS

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12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Since we successfully obtained a fused perfluoro (benzofuran) from perfluoro (dicyclohexyl ether), reductive defluorination of the perfluorinated ethers containing three perfluoro (cyclohexyl) groups wbuld be interesting. The three isomers of o-, m-, and p- perfluoro (dicyclohexanoxyl cyclohexane) were prepared by liquid-phase direct fluorination of o-, m-, and p- diphenoxyl benzene. After several runs of liquid-phase direct fluorination, enough amount of o-perfluoro (dicyclohexanoxyl cyclohexane) was collected to carry out the following reductive defluorination. The reductive defluorination was carried out from -70 to 70 degree for 2 days, but the ortho-ether, however, kept unreacted. One of the reasons for that is perhaps steric hindrance. Reductive defluorination of the meta- and para- ethers are under investigation.

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Second Annual Technical Report

to

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Washington, DC 20332

ELEMENTAL FLUORINE BASED SYNTHESES OF PENTAFLUORO PHENYL AND OTHER AROMATIC PERFLUOROPOLYETHER POLYMERS

Grant Number F49620-92-J-0104

February 1, 1993 - January 31, 1994

Presented by

Professor Richard J. Lagow

Department of Chemistry

The University of Texas at Austin

Austin, Texas 78712

TEL (512) 471-1032

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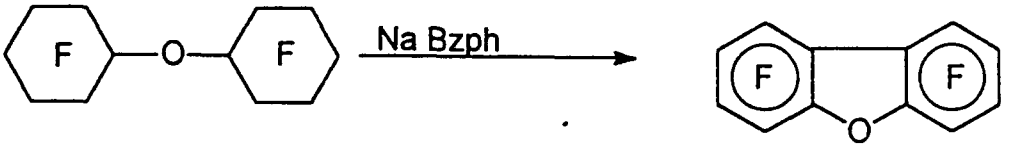
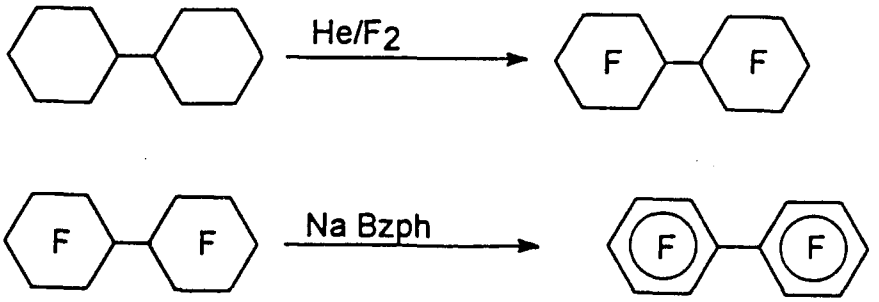
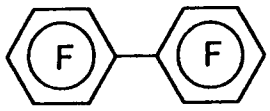
In last annual technical report, reductive defluorination of perfluoro(dicyclohexylether) was carried out with sodium benzophenone and the two perfluoro(cyclohexyl) groups were interestingly fused to form perfluoro(bezofuran). What about other perfluoro(dicyclohexyl) compounds ? Will they form fused products or other interesting compounds after the reductive defluorination ?

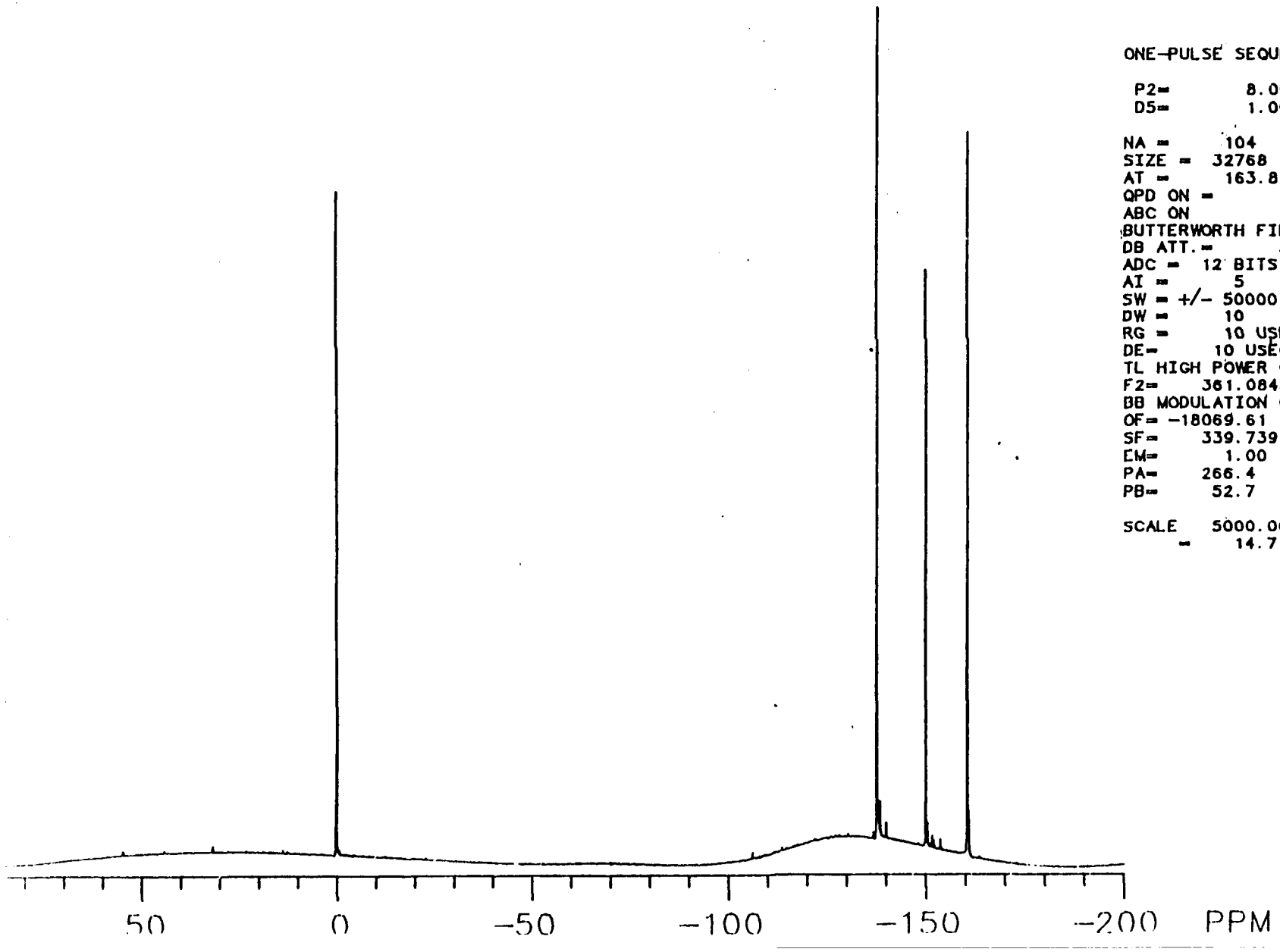


Perfluoro(dicyclohexyl) was prepared in 91% yield by liquid-phase direct fluorination of dicyclohexyl. Reductive defluorination of the perfluorinated compound produced a nonfused product, perfluoro(diphenyl), other than a fused product.



311 . 002 MJB 06MAY94
ING, CFCL3, CDCL3, F19





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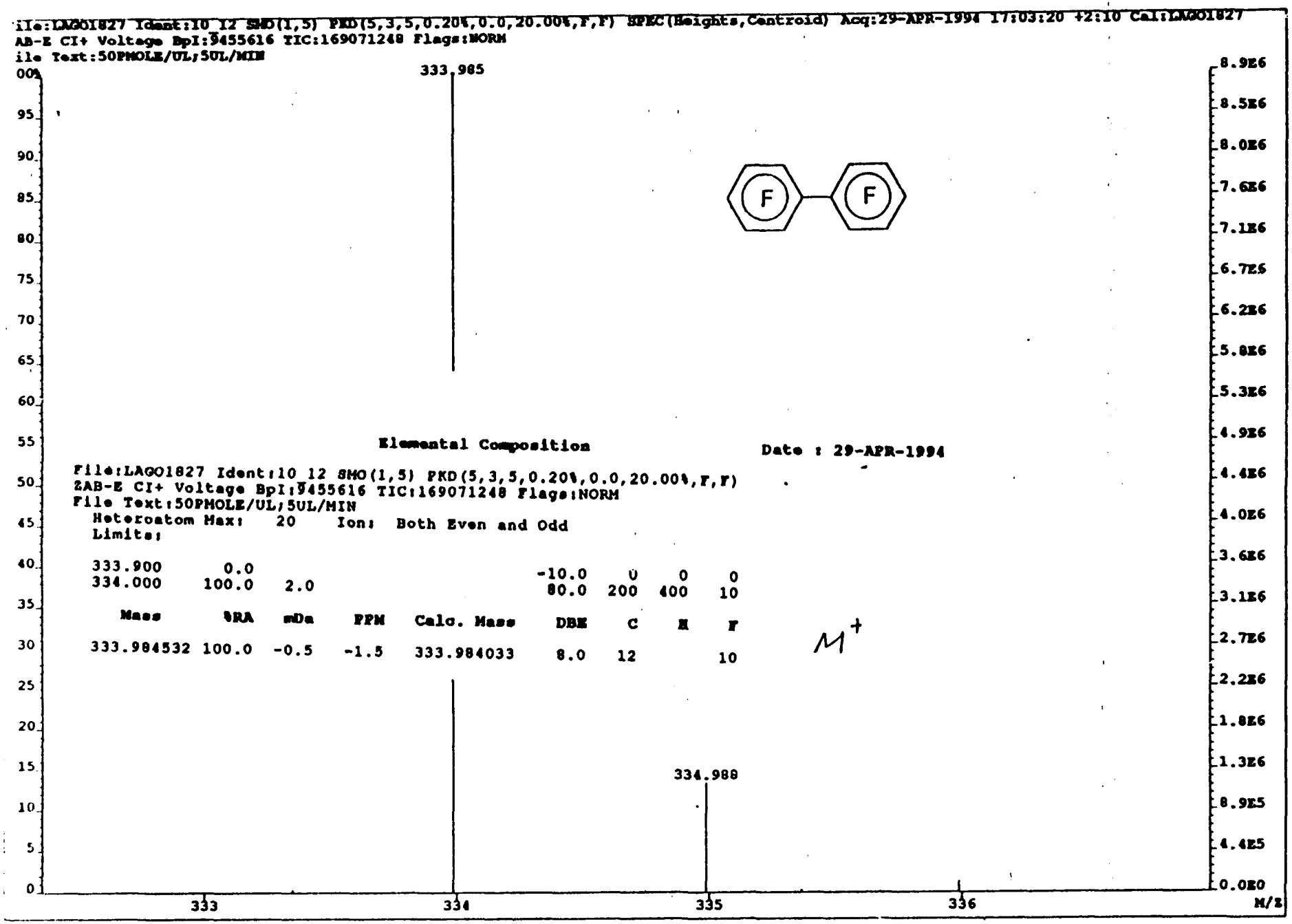
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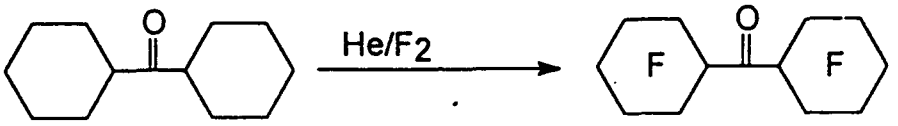
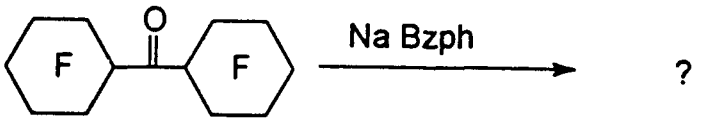
Perfluoro(dicyclohexyl) ketone was prepared in 82% yield by liquid-phase direct fluorination of dicyclohexyl ketone. Reductive defluorination of the perfluorinated ketone is under investigation.





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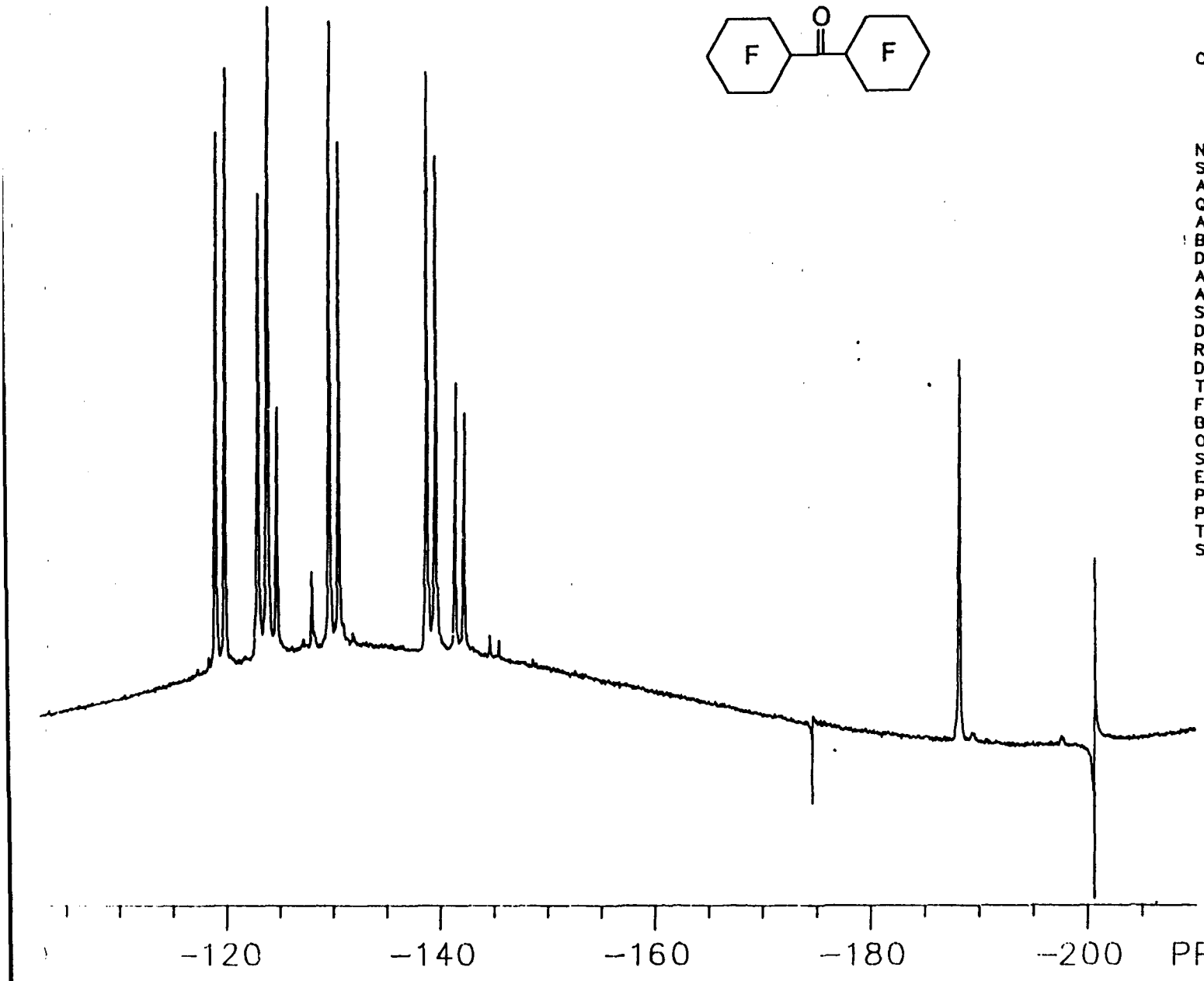
UNG, CFCL3, CDCL3, F19, 20C



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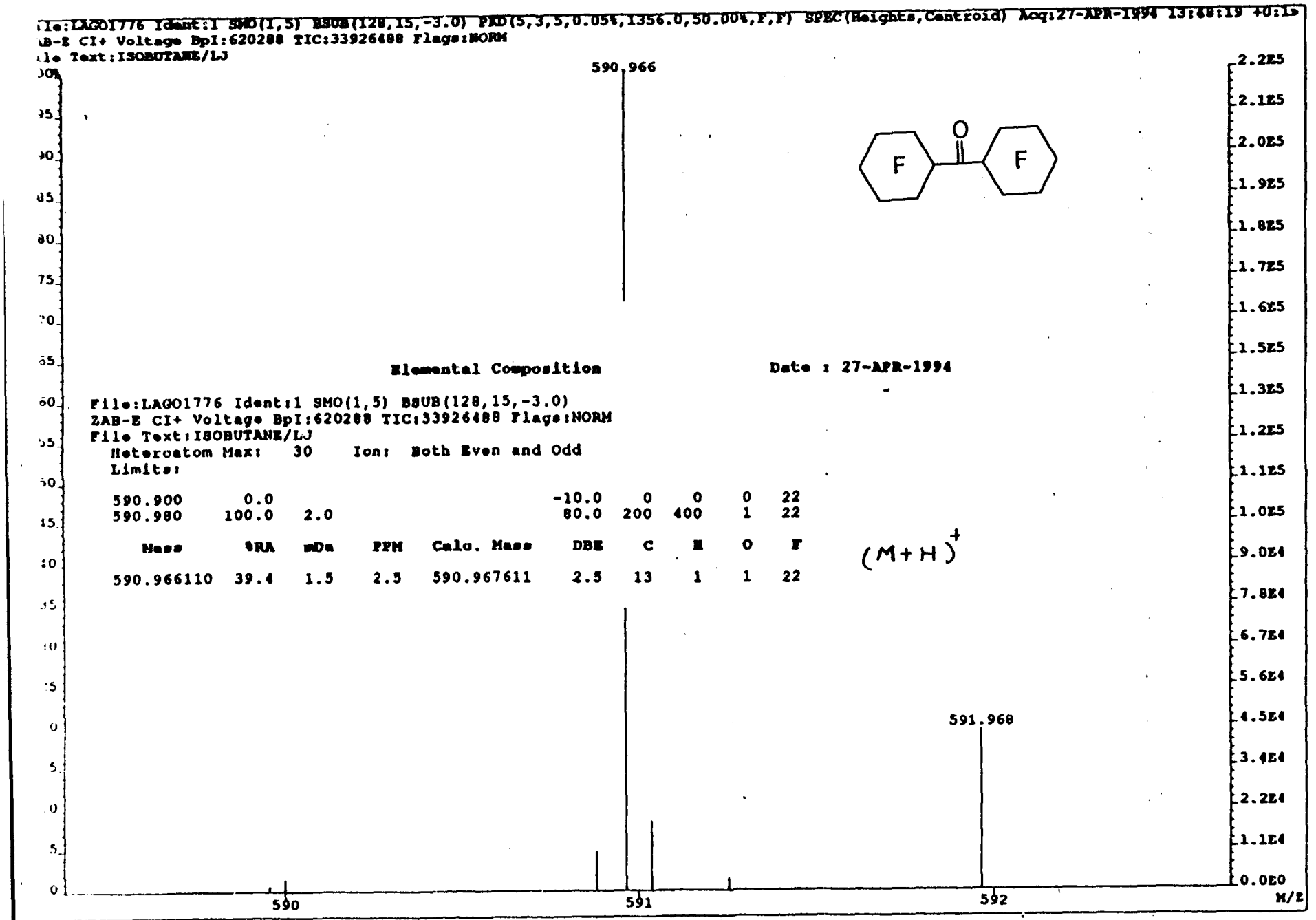
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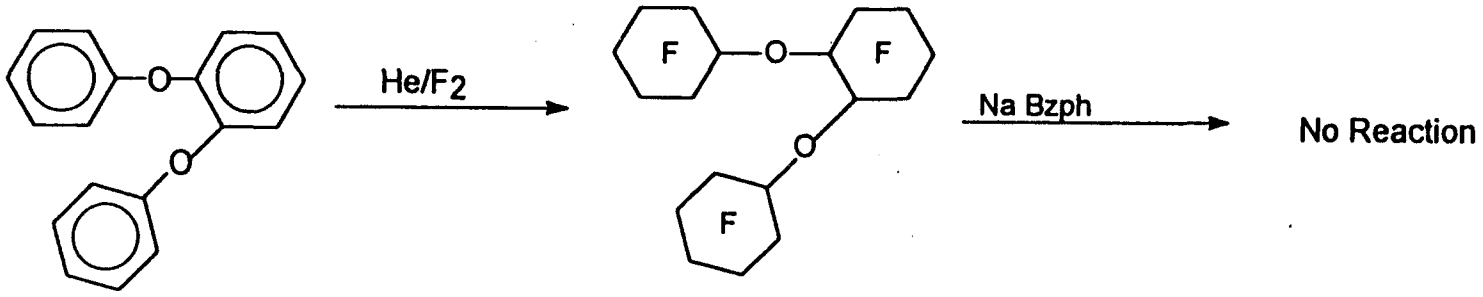
(M+H)+
591.968
590
591
592
M/z

Since we successfully obtained a fused perfluoro(benzofuran) from perfluoro(dicyclohexyl ether), reductive defluorination of the perfluorinated ethers containing three perfluoro(cyclohexyl) groups would be interesting. The three isomers of o-, m-, and p-perfluoro(dicyclohexanoxyl cyclohexane) were prepared by liquid-phase direct fluorination of o-, m-, and p- diphenoxyl benzene. After several run of liquid-phase direct fluorination, enough amount of o-perfluoro(dicyclohexanoxyl cyclohexane) was collected to carry out the following reductive defluorination. The reductive defluorination was carried out from -70 to 70 °C for 2 days, but the ortho-ether, however, kept unreacted. One of the reasons for that is perhaps steric hindrance. Reductive defluorination of the meta- and para- ethers are under investigation.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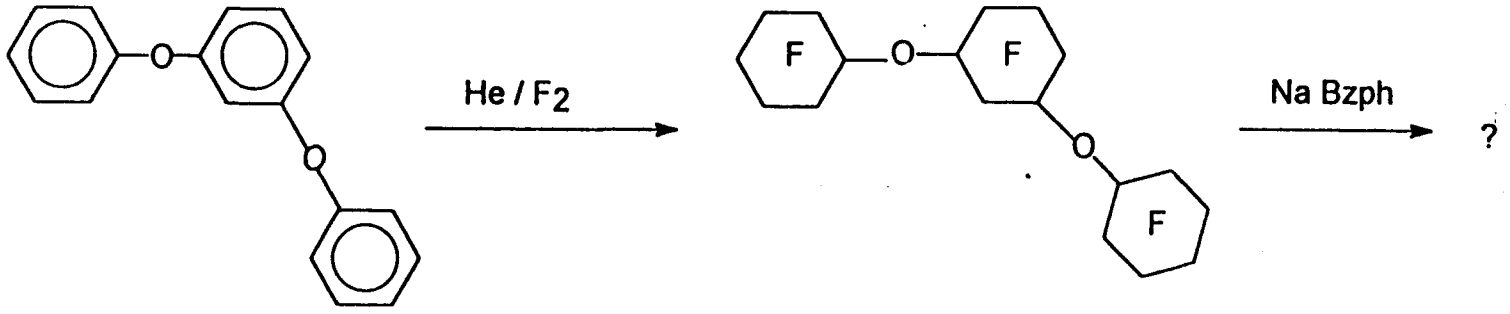
O
F
Na Bzph
No Reaction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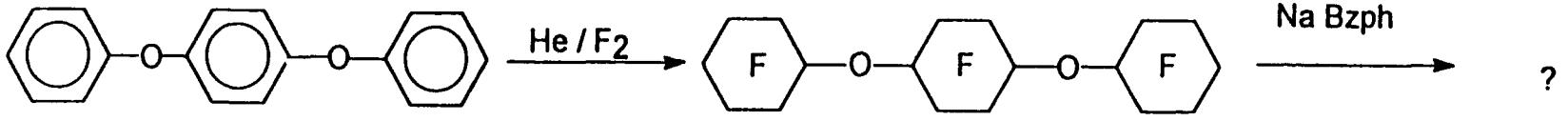
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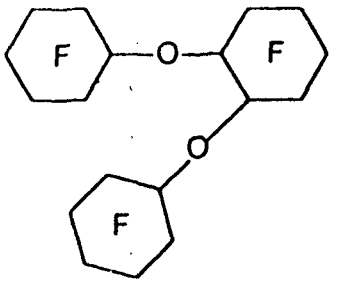

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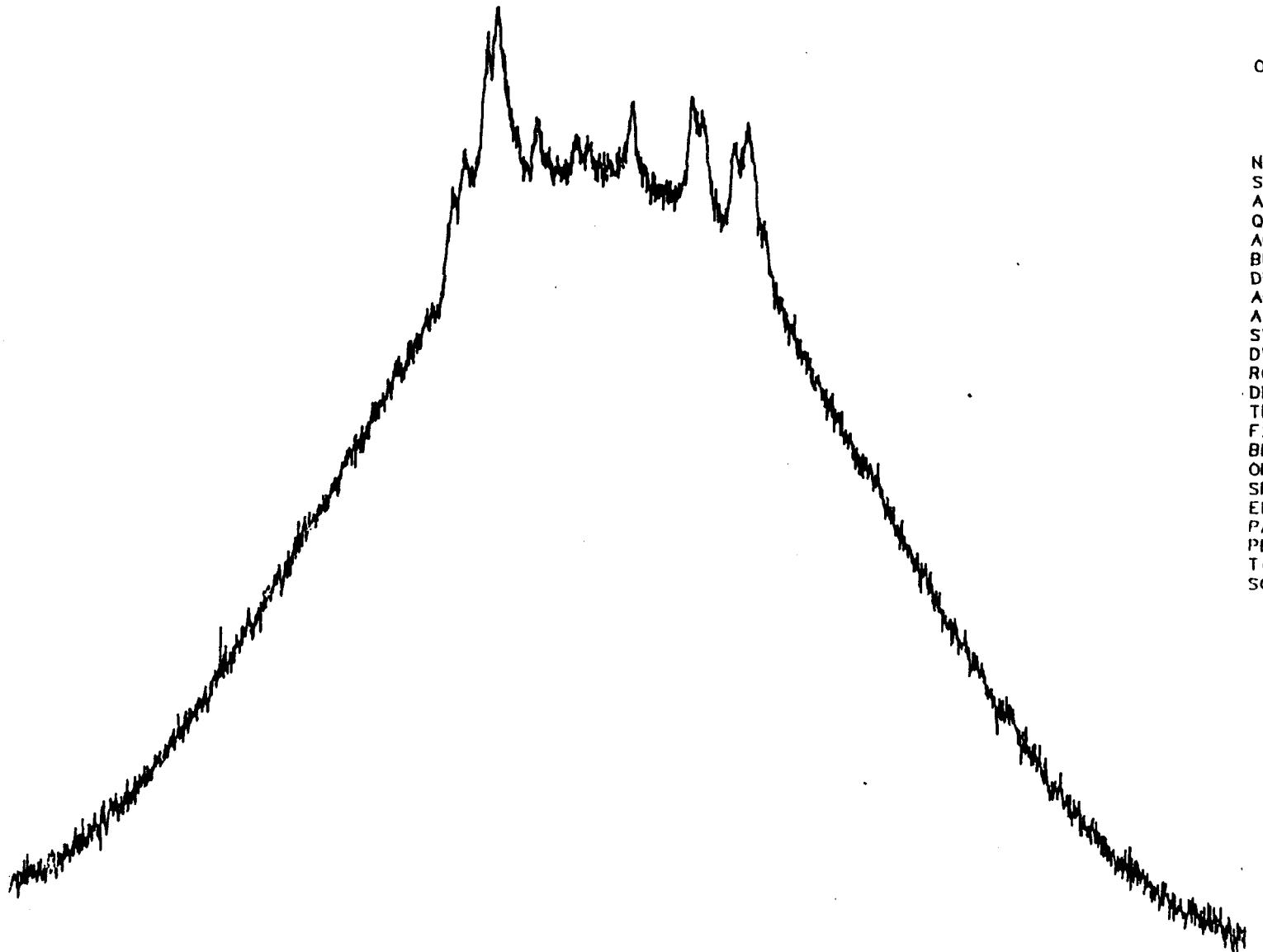

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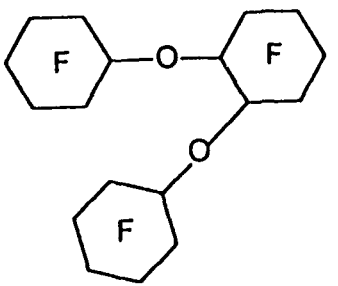

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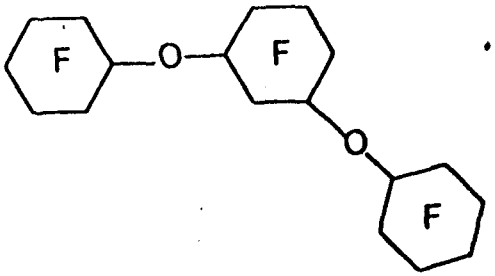
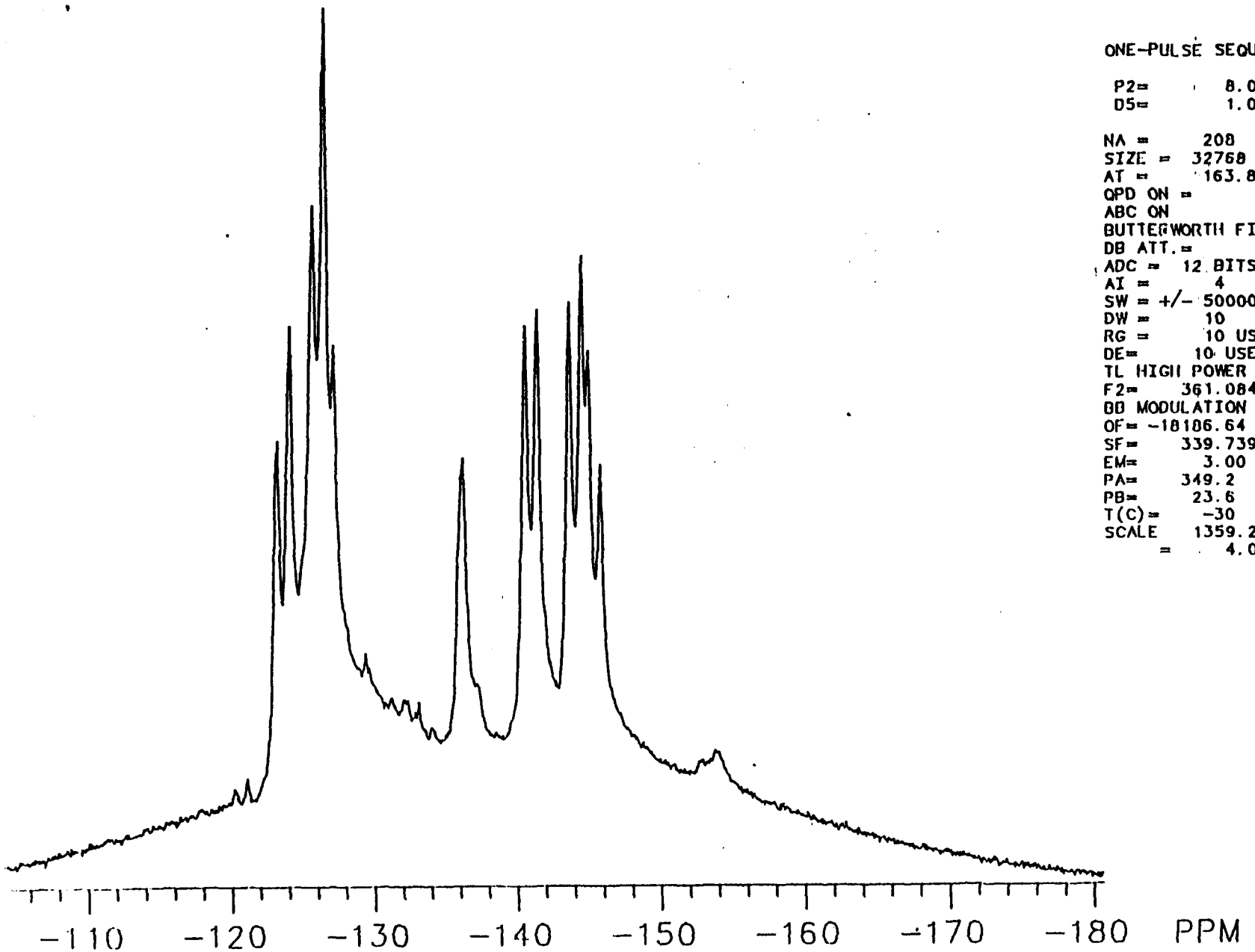
IG, CDCL3, CFCL3, F19, -30





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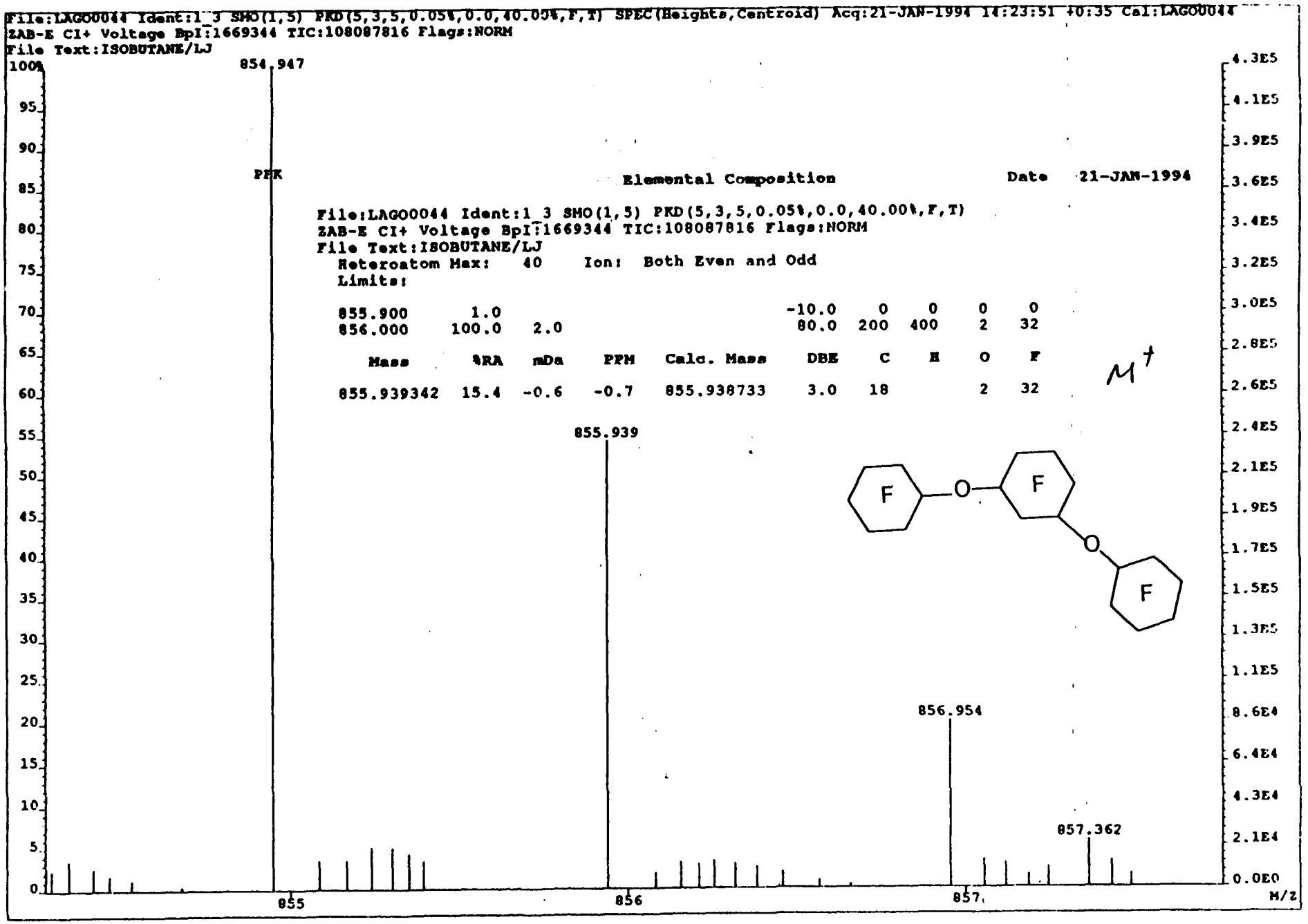
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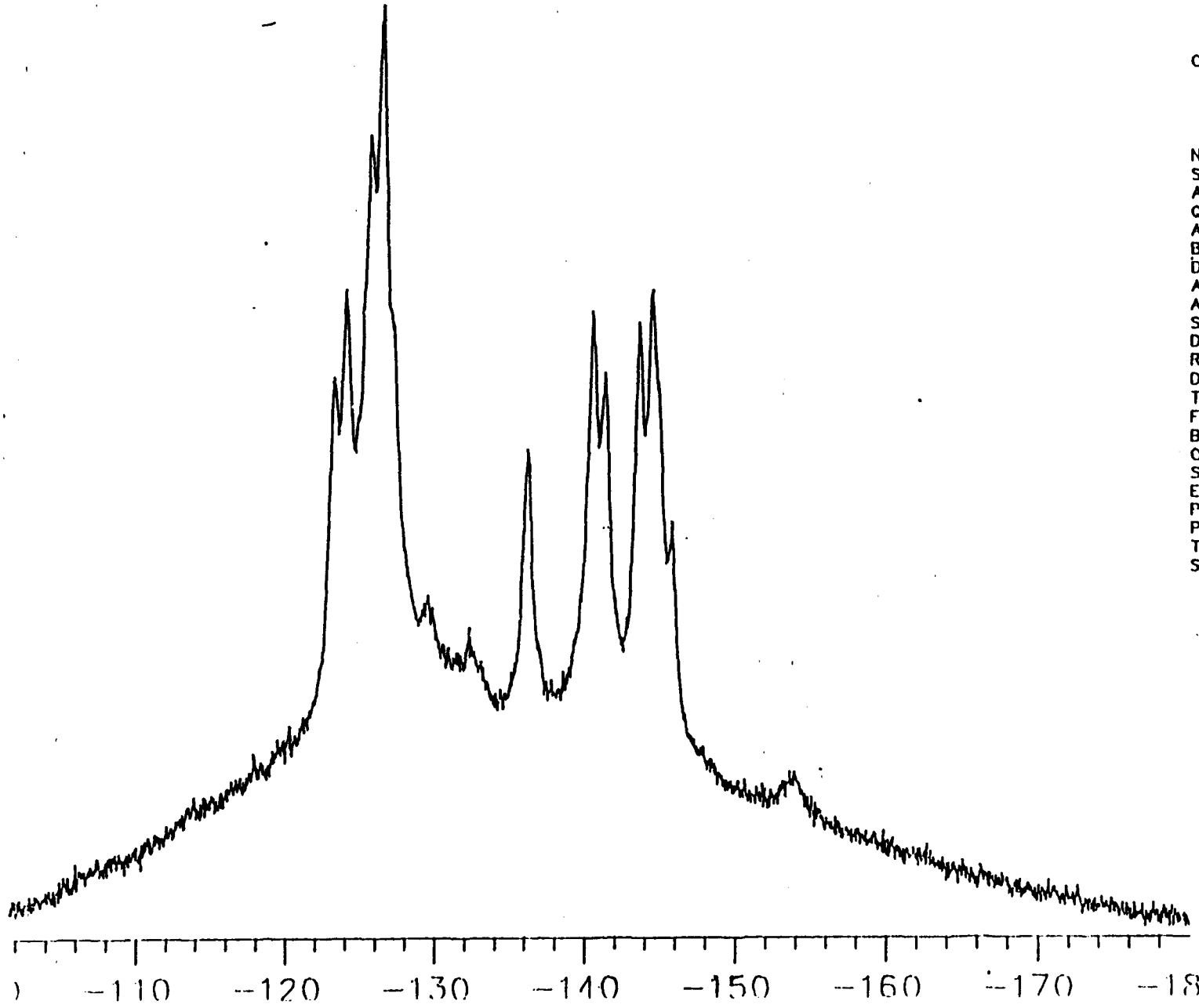

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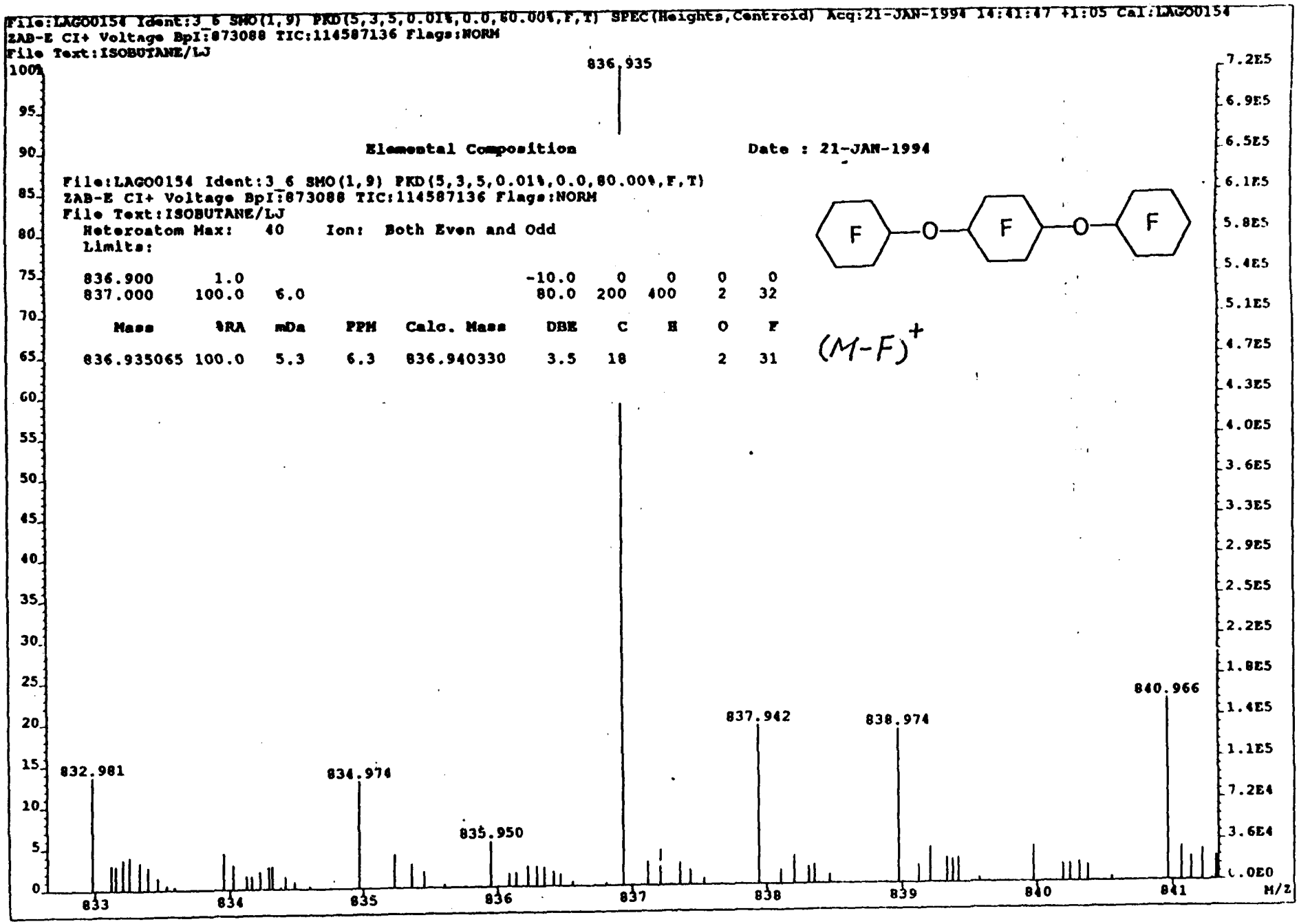
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Date : 21-JAN-1994
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ZAB-E CI+ Voltage BpI:873088 TIC:114587136 Flags:NORM
File Text:ISOBUTANE/LJ
Heteroatom Max: 40 Ion: Both Even and Odd
Limits:
836.900 1.0 -10.0 0 0 0 0
837.000 100.0 6.0 80.0 200 400 2 32
Mass %RA mDa PPM Calc. Mass DBE C H O F
836.935065 100.0 5.3 6.3 836.940330 3.5 18 2 31
F O F O F
(M-F)+
832.981
834.974
835.950
837.942
838.974
840.966
M/z

Synthesis of perfluoro(hexamethylcyclohexane-1,3,5-trione) was reported in last report. Now we want to show its unusual solid state conformation. The molecule is unusually flattened, as can be seen from the sum of the six ring torsion angles 31 + 18 + 14 + 32 + 18 + 12 = 125 °. By contrast, the sum of the ring torsional angles in cyclohexane and hexamethylcyclohexane-1,3,5-trione are 336 and 192 °, respectively. In comparison with boat conformation of hexamethylcyclohexane-1,3,5-trione, conformation of the perfluorinated analogue is a twisted boat in order to avoid the three axial trifluoromethyl groups, coming much too close and creating a serious strain.

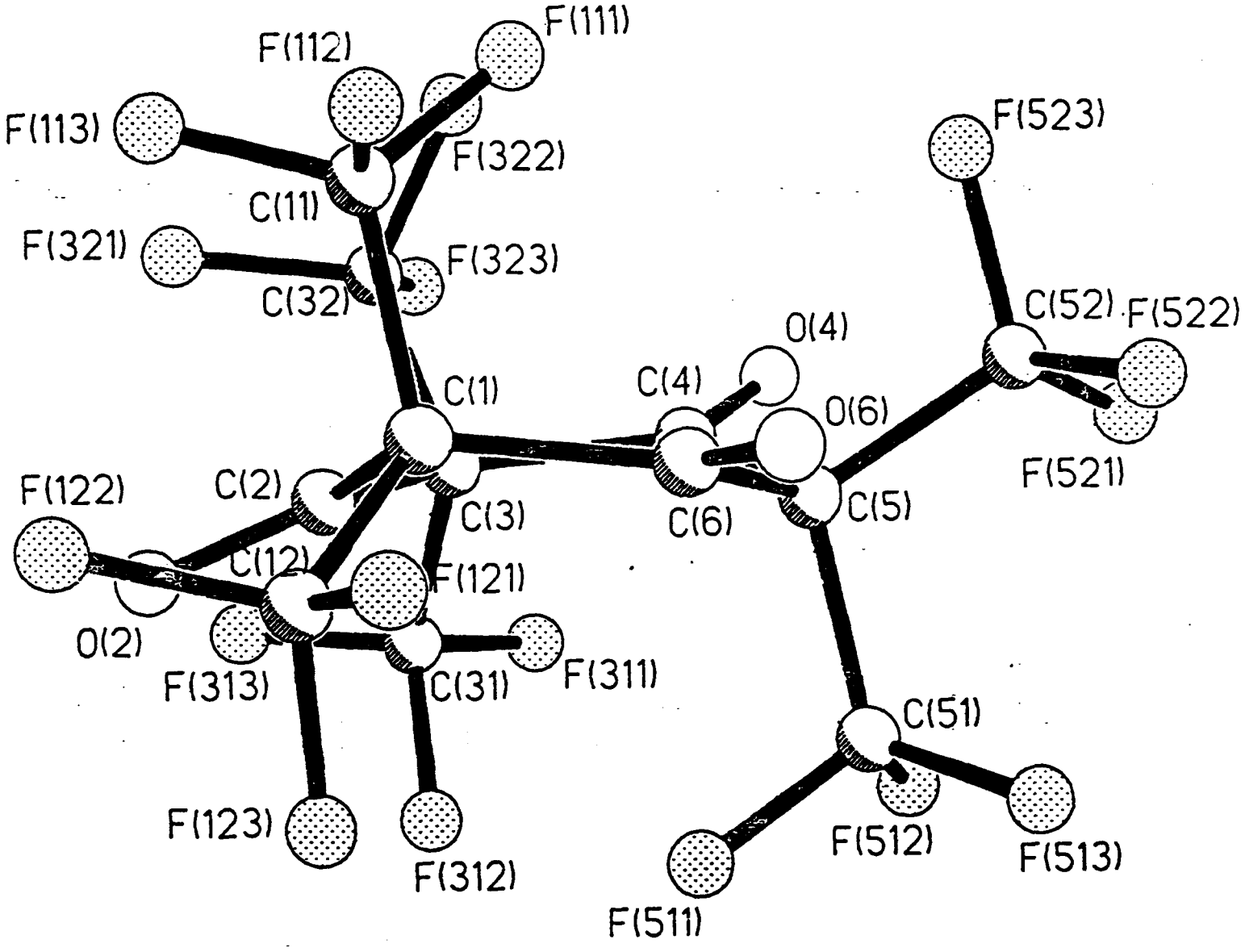
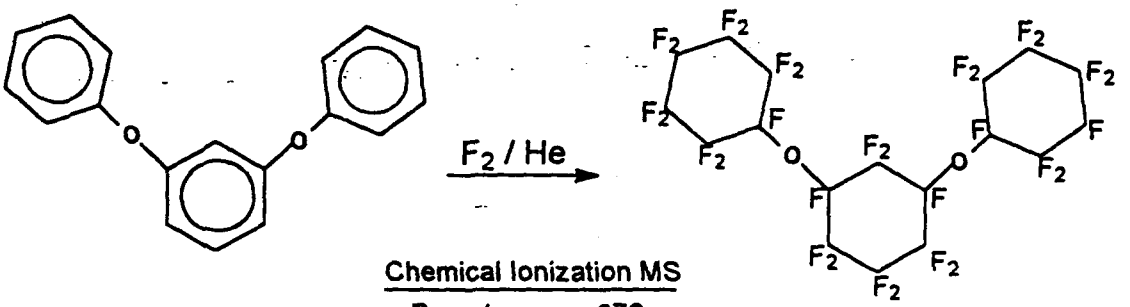


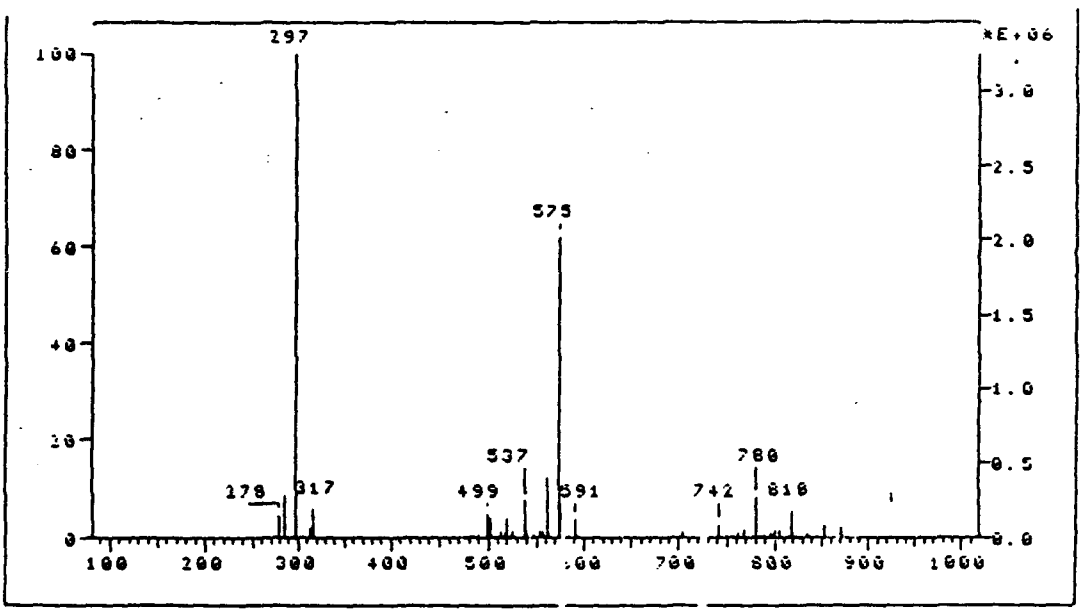
Fig.1. Molecular structure of ~~$C_{12}F_{18}O_3$~~ (1).;
Selected bond lengths (Å):C(2)-O(2) 1.188(5), C(4)-O(4) 1.179(5), C(6)-O(6) 1.178(5); bond angles (°): C(2)-C(1)-C(6) 115.7(4), C(2)-C(3)-C(4) 115.8(4), C(6)-C(5)-C(4) 116.0(4); torsion angles (°): C(6)-C(1)-C(2)-C(3) -30.8(6), C(1)-C(2)-C(3)-C(4) 17.9(6), C(2)-C(3)-C(4)-C(5) 14.4(6), C(3)-C(4)-C(5)-C(6) -32.3(6), C(4)-C(5)-C(6)-C(1) 18.3(6), C(2)-C(1)-C(6)-C(5) 11.8(6).

Other homologs of diphenyl ether such as 1,3-, and 1,4- diphenoxy benzene have also been perfluorinated for subsequent reductive defluorination.

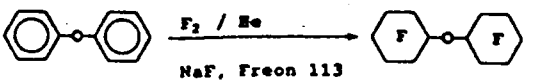


Chemical Ionization MS

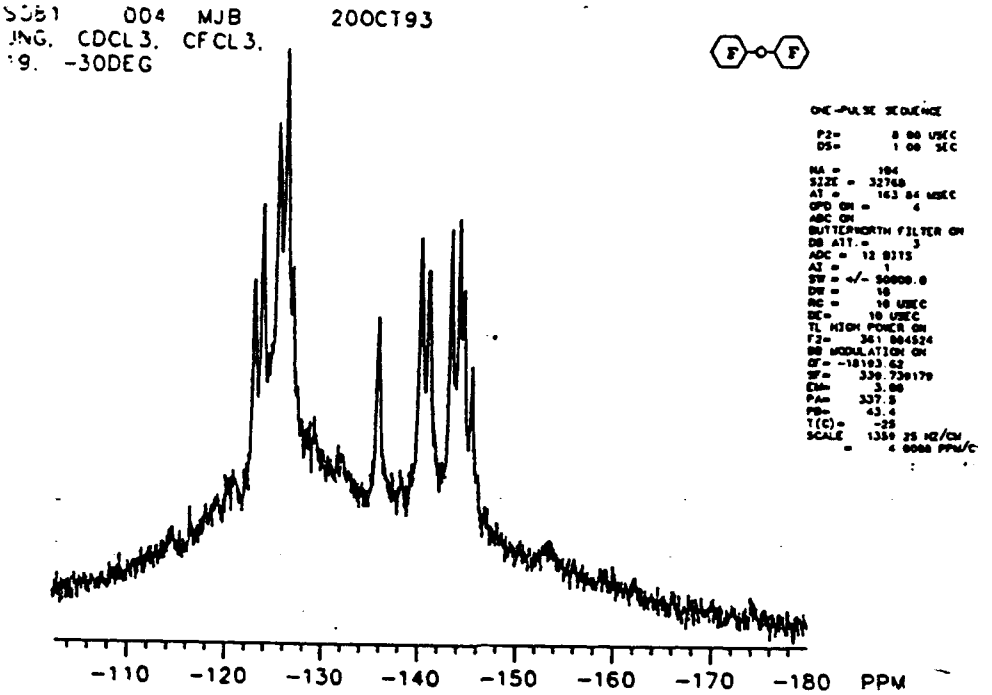
Parent - 872
P-F - 853
P- (C_6F_{11}) - 591
P- ($C_6F_{11}O$) - 575
P- ($C_6F_{11}O$-C_6F_{10}) - 297
P- 2x ($C_6F_{11}O$) - 278



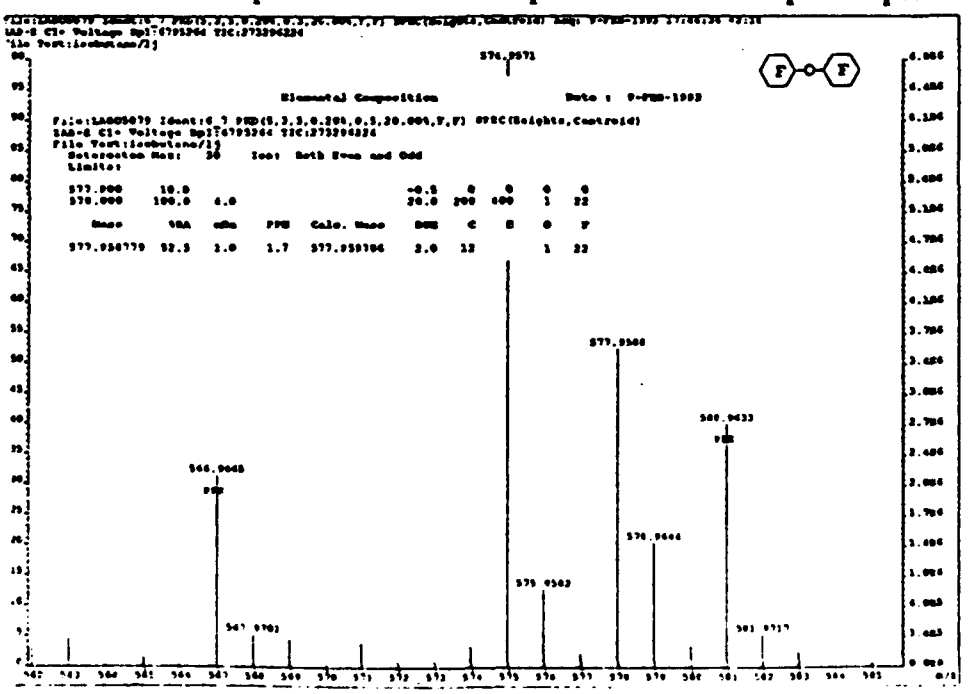
We have done considerable work on defluorination of cyclohexyl substituted fluorine compounds. This work is now becoming more and more successful and has been aided very considerably by the publication of a full manuscript by Dr. Guido Pez on methods using sodium benzophenone (J. Org. Chem. 1992, 57, 2856-2860). Yet removing extra fluorines remains one of the problems that we are in the process of solving. There are a series of sodium substituted defluorination reagents. One of the mildest is sodium phenylthiolate by Professor David McNicol of Glasgow. The synthesis of perfluoro biscyclohexyl ether was accomplished in 83% yield.

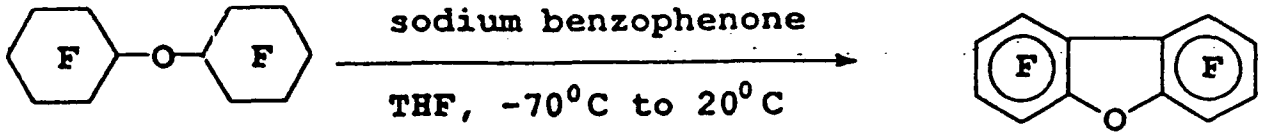


The ^{19}F NMR Spectrum of Biscyclohexyl Ether

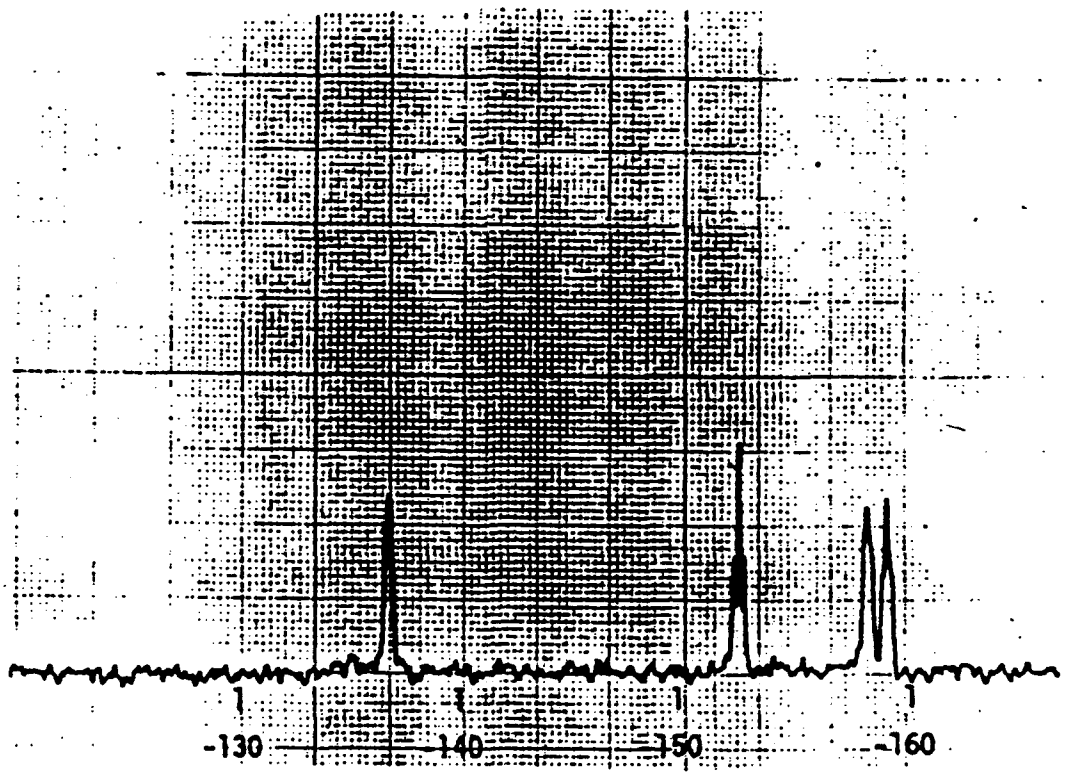


The high resolution mass spectrum of the final product contains a parent peak at 577.9588.





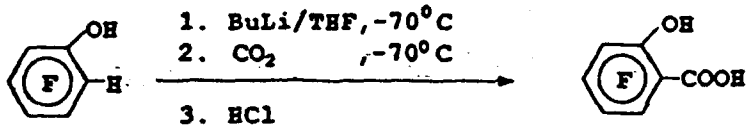
^{19}F NMR Spectrum of the Defluorinated Product



This is a very interesting case. Two extra fluorine were removed and we obtained the very interesting perfluoro furan compound shown above. We are now think we have been successful in applying it to a four-membered perfluoro cyclohexyl ether (page 7) (degree of polymerization four) and we shall see if we get the furan structure on that one as well. If successful it should produce an oligomer containing three furan units.

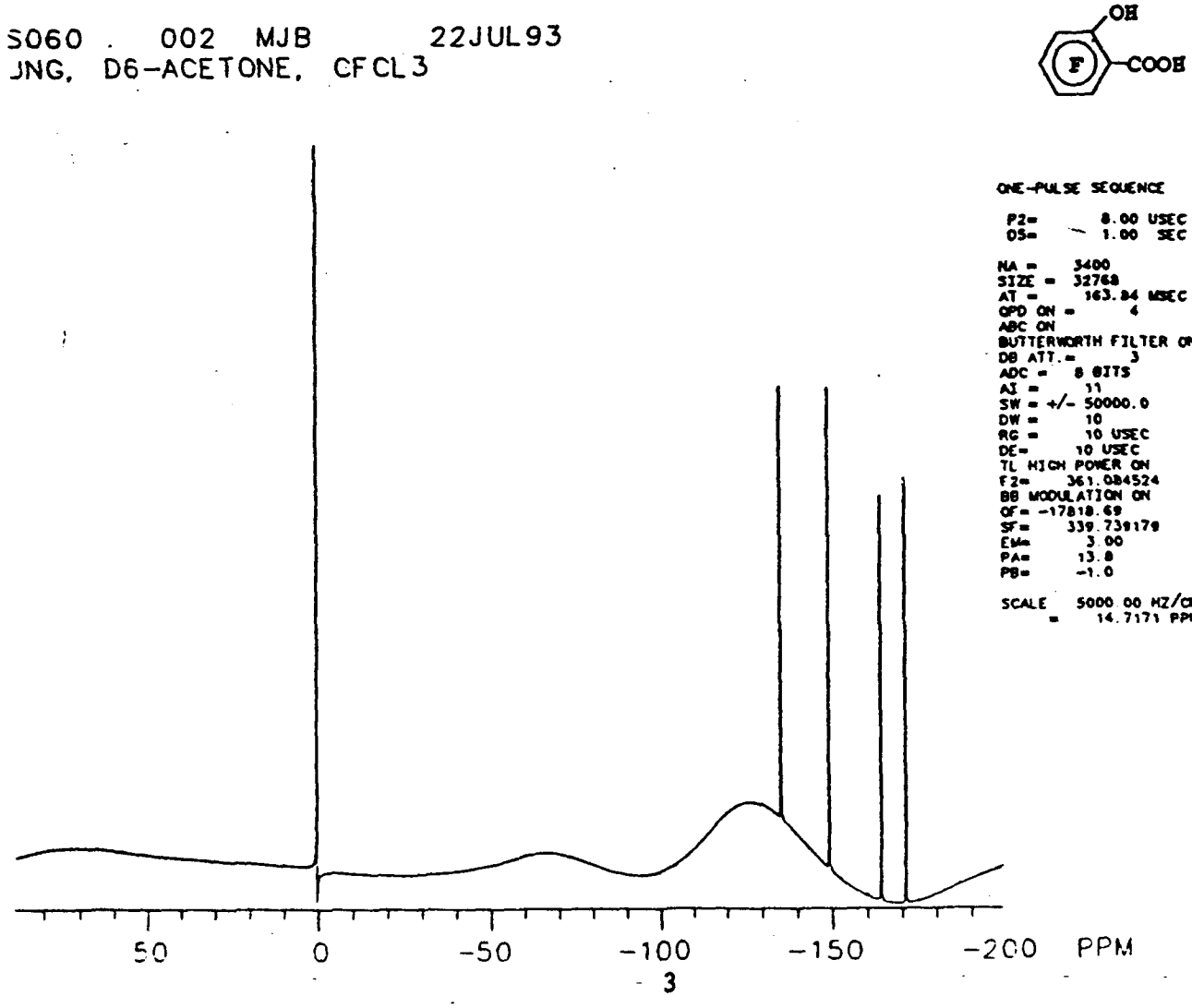
Preparation of Perfluorinated Salicylic Acid

By first synthesizing in 60% yield the perfluoro aromatic precursor, namely 1-hydrotetrafluorophenol, we then synthesized 2,3,4,5-tetrafluoro-6-hydroxybenzoic acid by the following procedure:

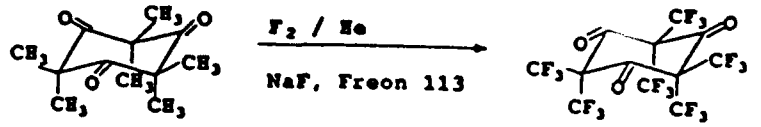


This step resulted in perfluorinated salicylic acid in 90% yield. Esters of salicylic acid are currently the most widely used lubrication antifriction additives to motor oils. We are now experimenting with making substituted hydrocarbon ester tails with one chlorine to make the product more soluble in polyalphaolefins and petroleum oils.

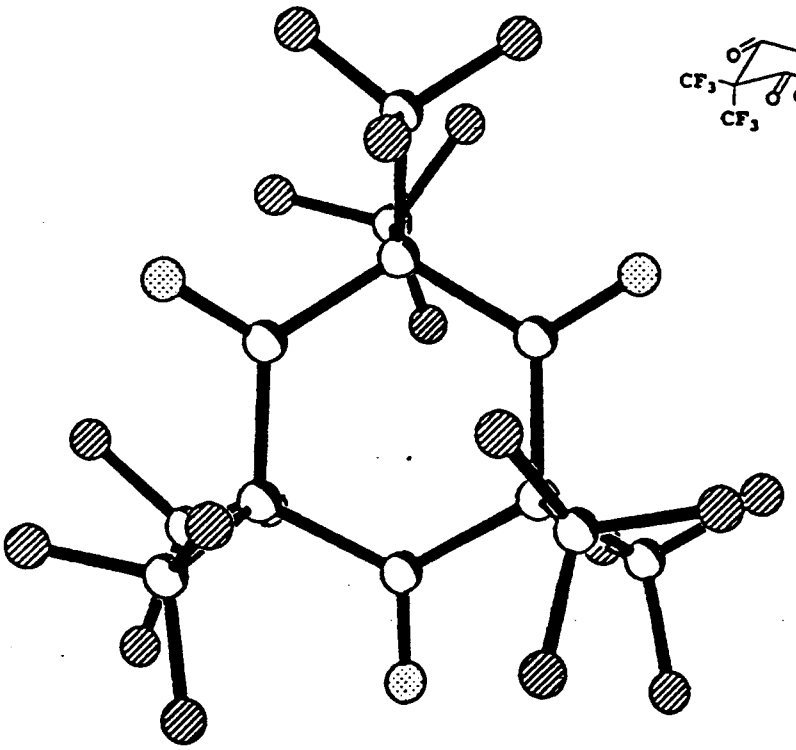
The ^{19}F NMR Spectrum of Perfluoro Salicylic Acid

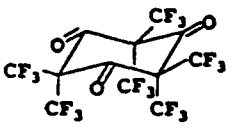


Very unusual perfluoro polyketone structures have been prepared by Dr. Kuangsen Sung. In particular, Dr. Sung has prepared a perfluorinated ketone from a hydrocarbon starting material in 72% yield.

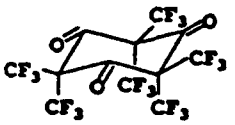


We have also obtained the crystal structure of this unusual new fluorocarbon material.

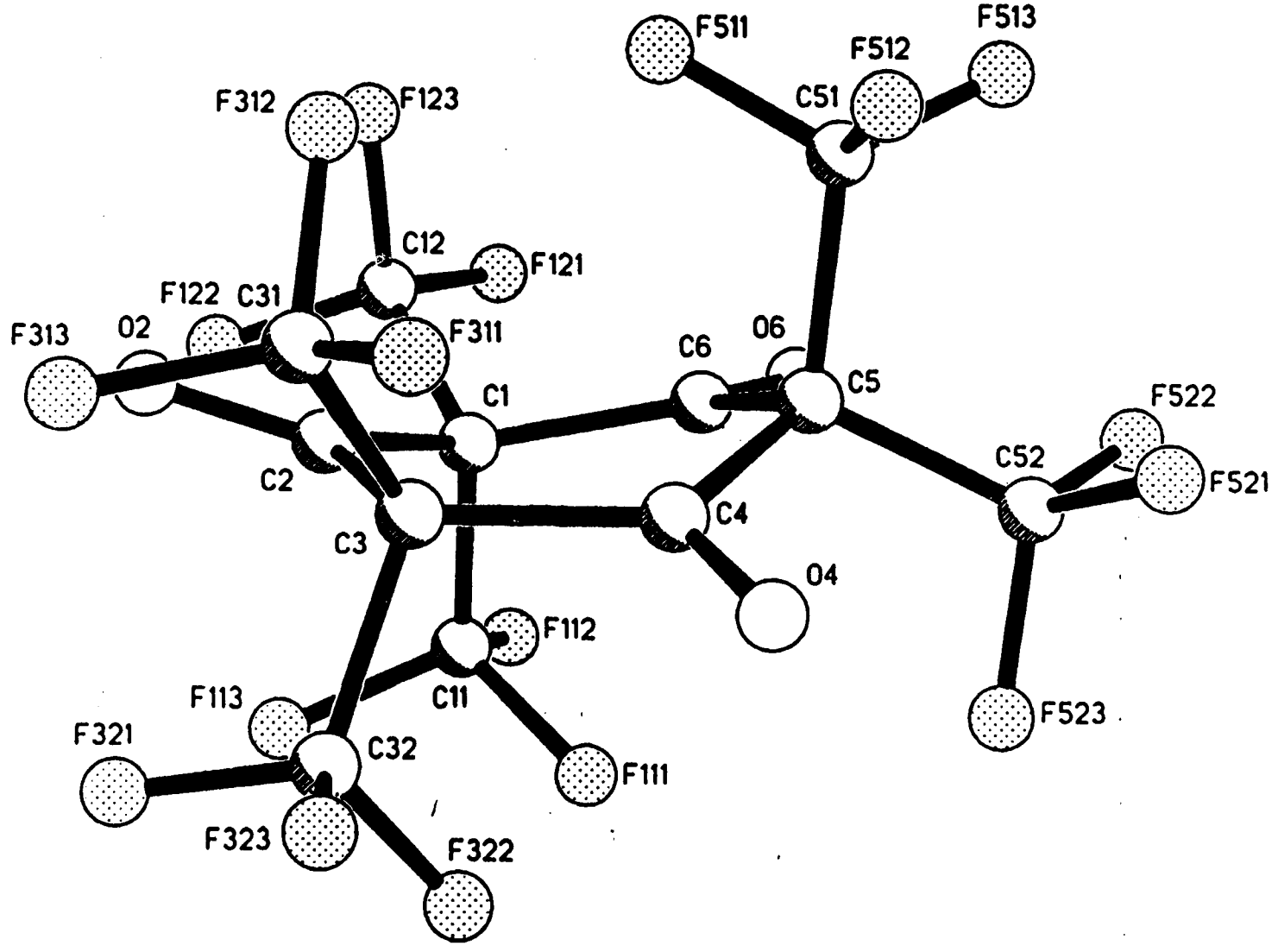




The ^{19}F NMR Spectrum of the Perfluorinated Ketone

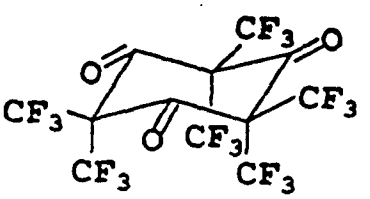


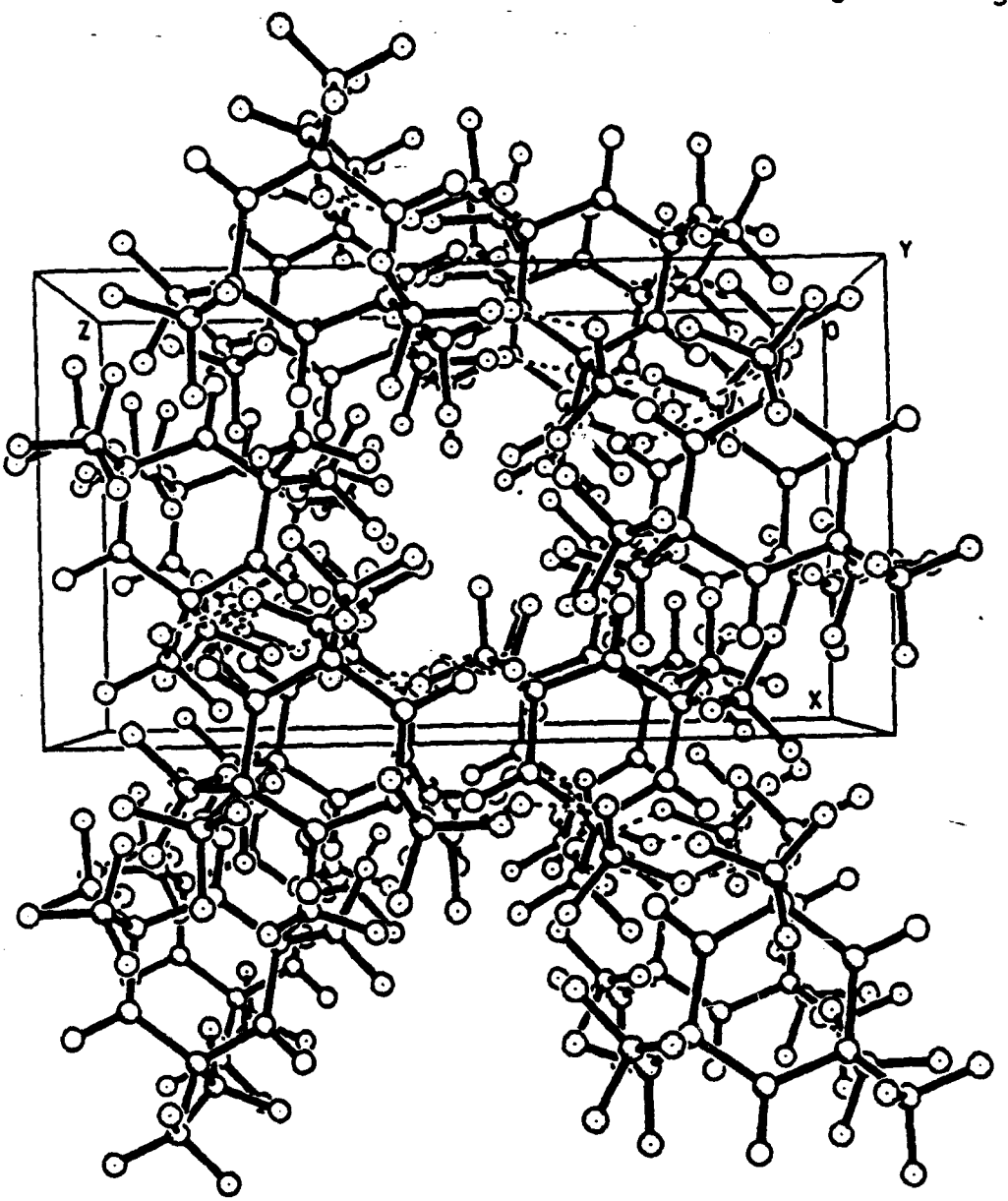
C12 F18 O3


F511
F513
F512
F312
F123
C51
C12
F121
F122
C31
F313
O2
F311
C6
O6
C1
C5
F522
C2
C52
F521
C4
C3
O4
F112
C11
F113
F523
F321
C32
F111
F323
F322

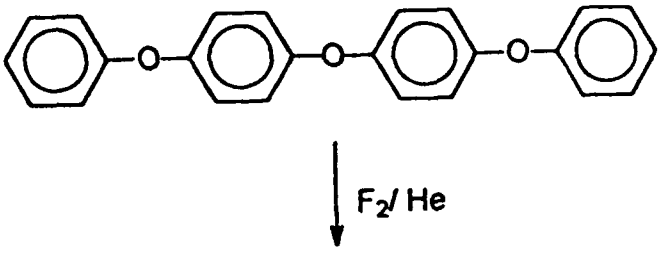
We think the zeolitic solid state structure of this very interesting perfluoro polyketone is most unusual and there may be interesting chemistry associated with the pockets of such a material.

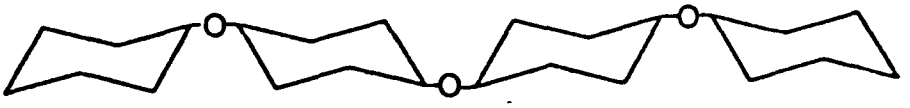
Zeolitic Structure of





A number of other perfluoro organometallic compounds have been prepared for their conversion to perfluoro aromatic analogs.

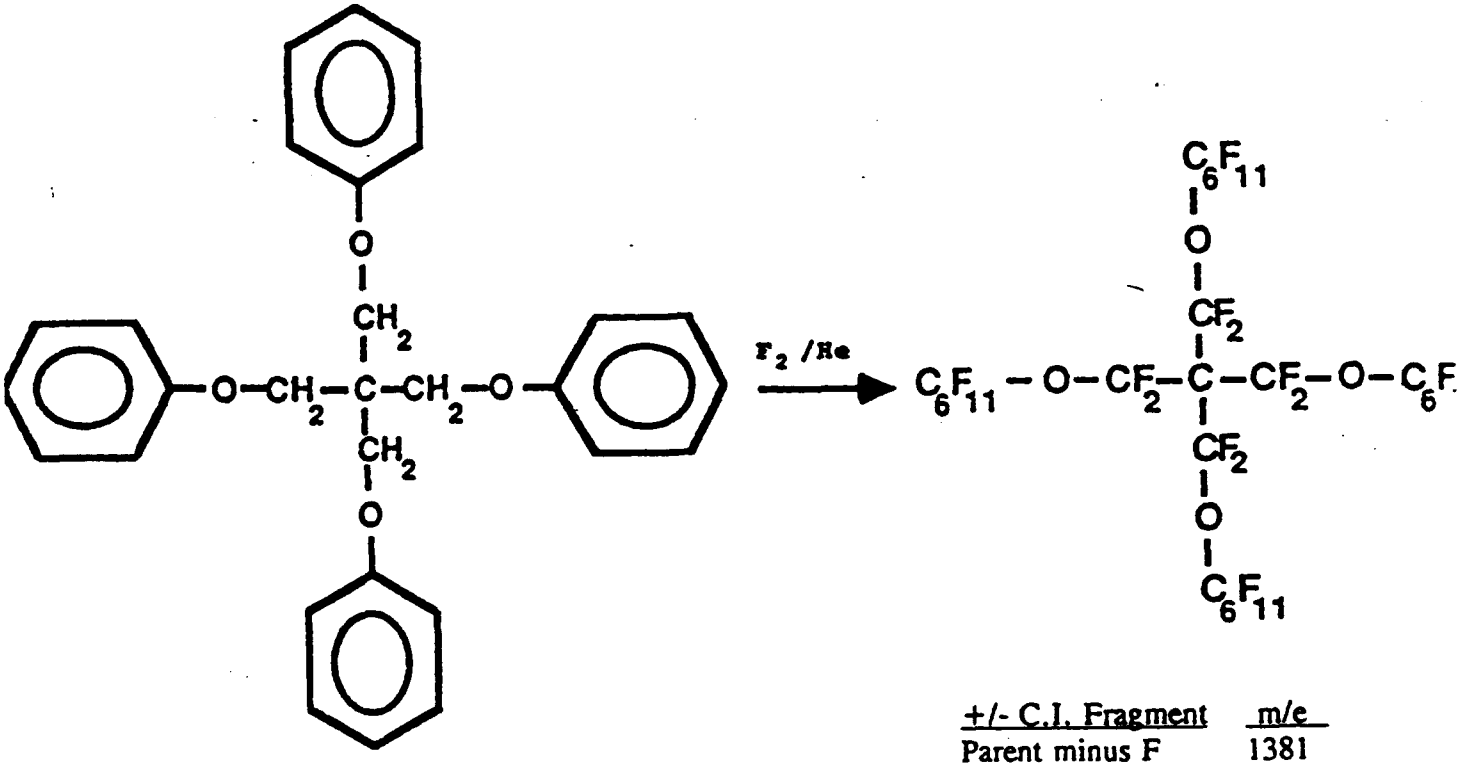




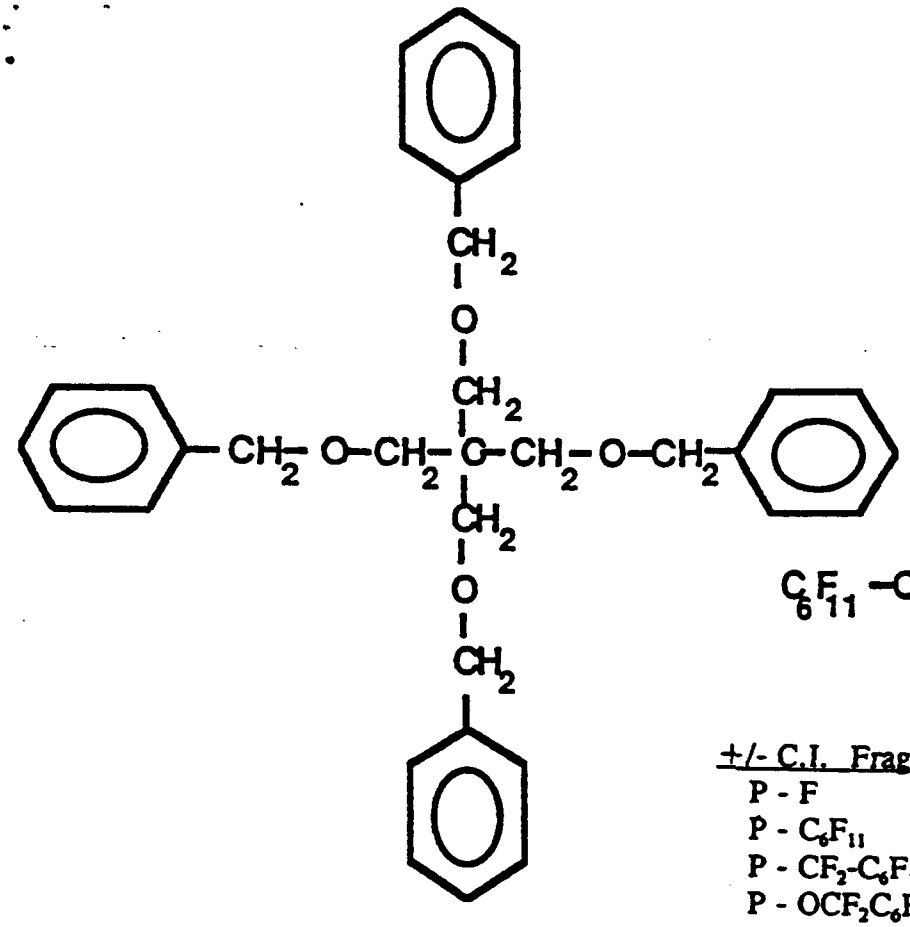
F

+/- C.I. Fragment	m/e
P - F	1115
P - C_6F_{11}	853
P - OC_6F_{11}	837
P - $C_6F_{10}OC_6F_{11}$	575
P - $OC_6F_{10}OC_6F_{11}$	559

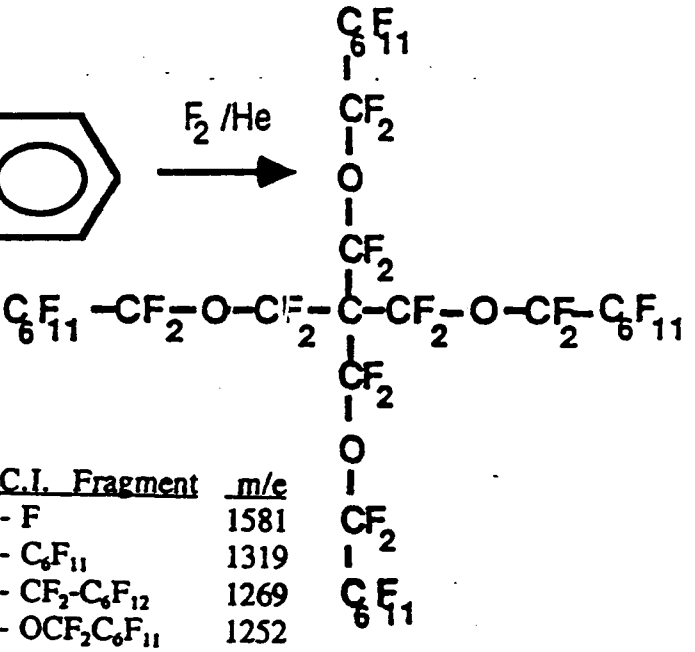
This structure is very interesting for under certain circumstances we hope to get the furan structure and with other reagents we hope to get the perfluorinated phenyl material. The perfluorinated cyclohexyl analog is already in hand.



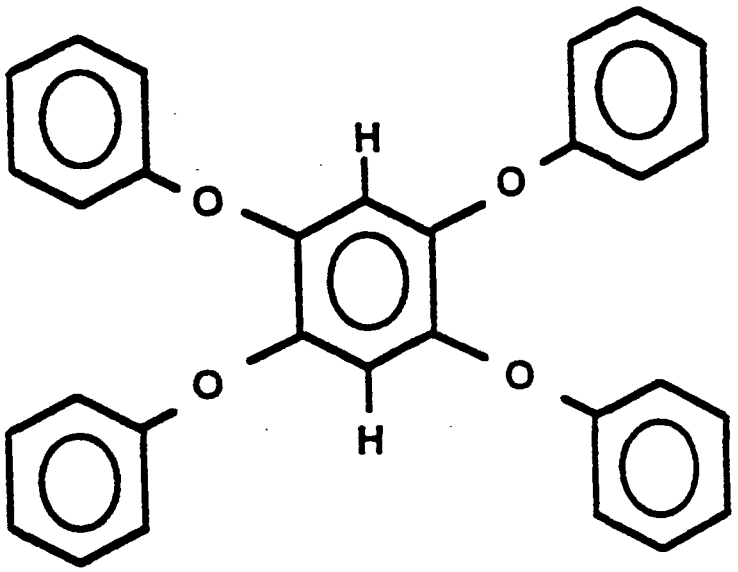
+/- C.I. Fragment	m/e
Parent minus F	1381
P - C_6F_{11}	1119
P - OC_6F_{11}	1103
P - CF_2-O-C_6F_{11}	1053



F_2 /He



+/- C.I. Fragment	m/e
P - F	1581
P - C_6F_{11}	1319
P - CF_2-C_6F_{12}	1269
P - $OCF_2C_6F_{11}$	1252

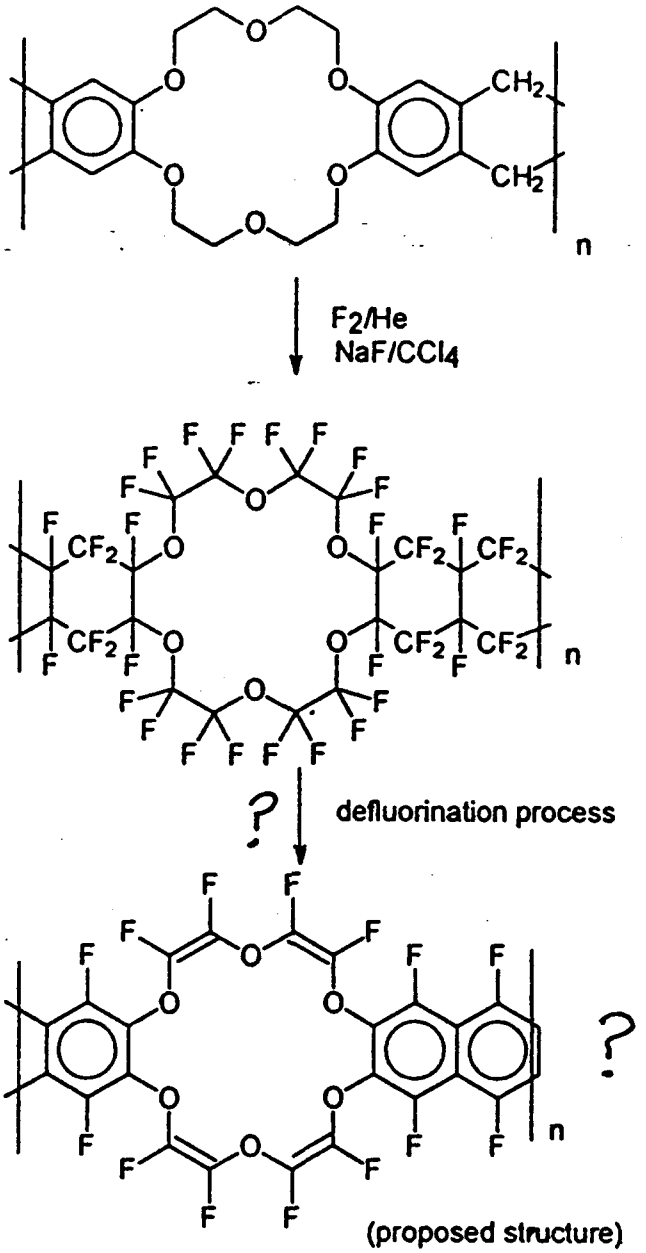


$C_6F_8(OC_6F_{11})_4$

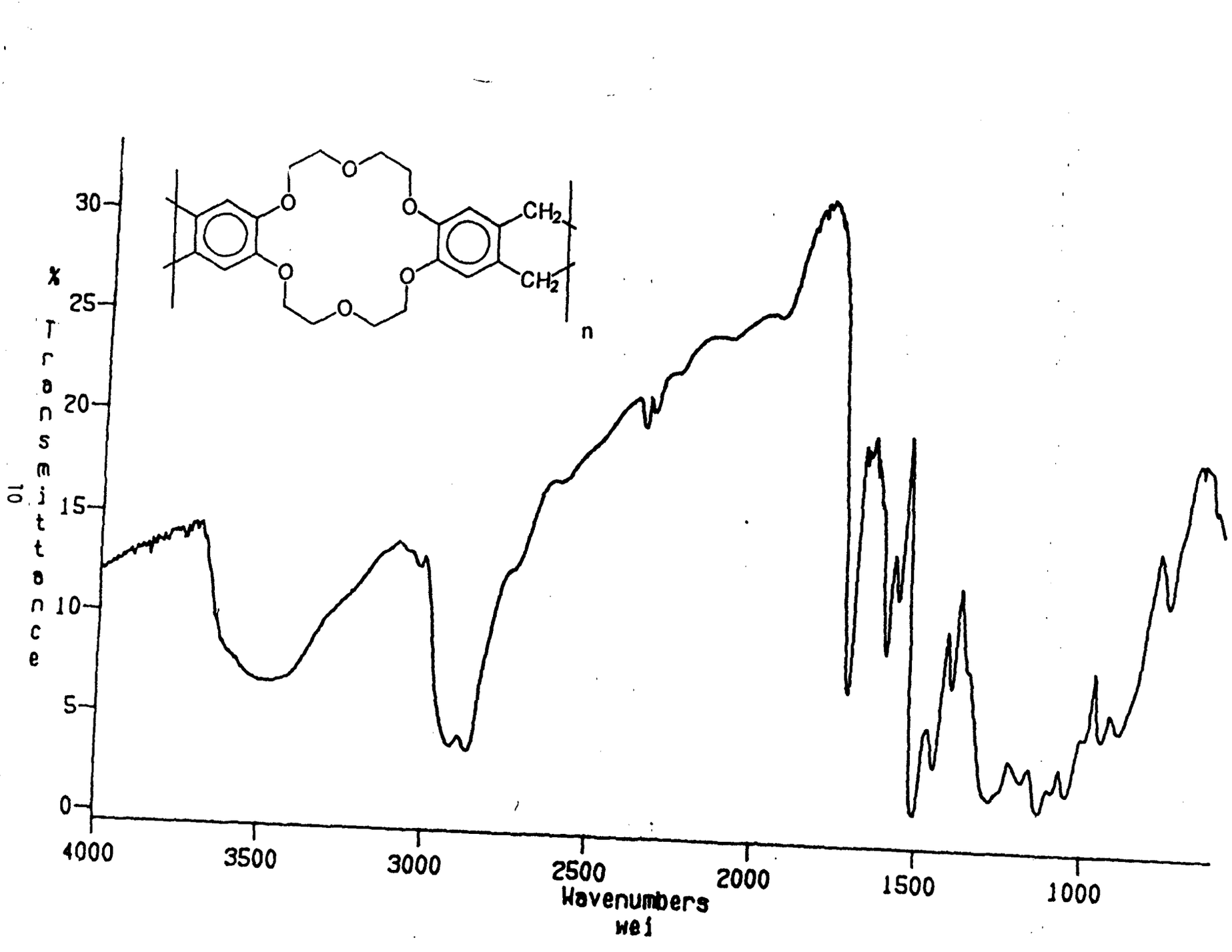
F_2 /He

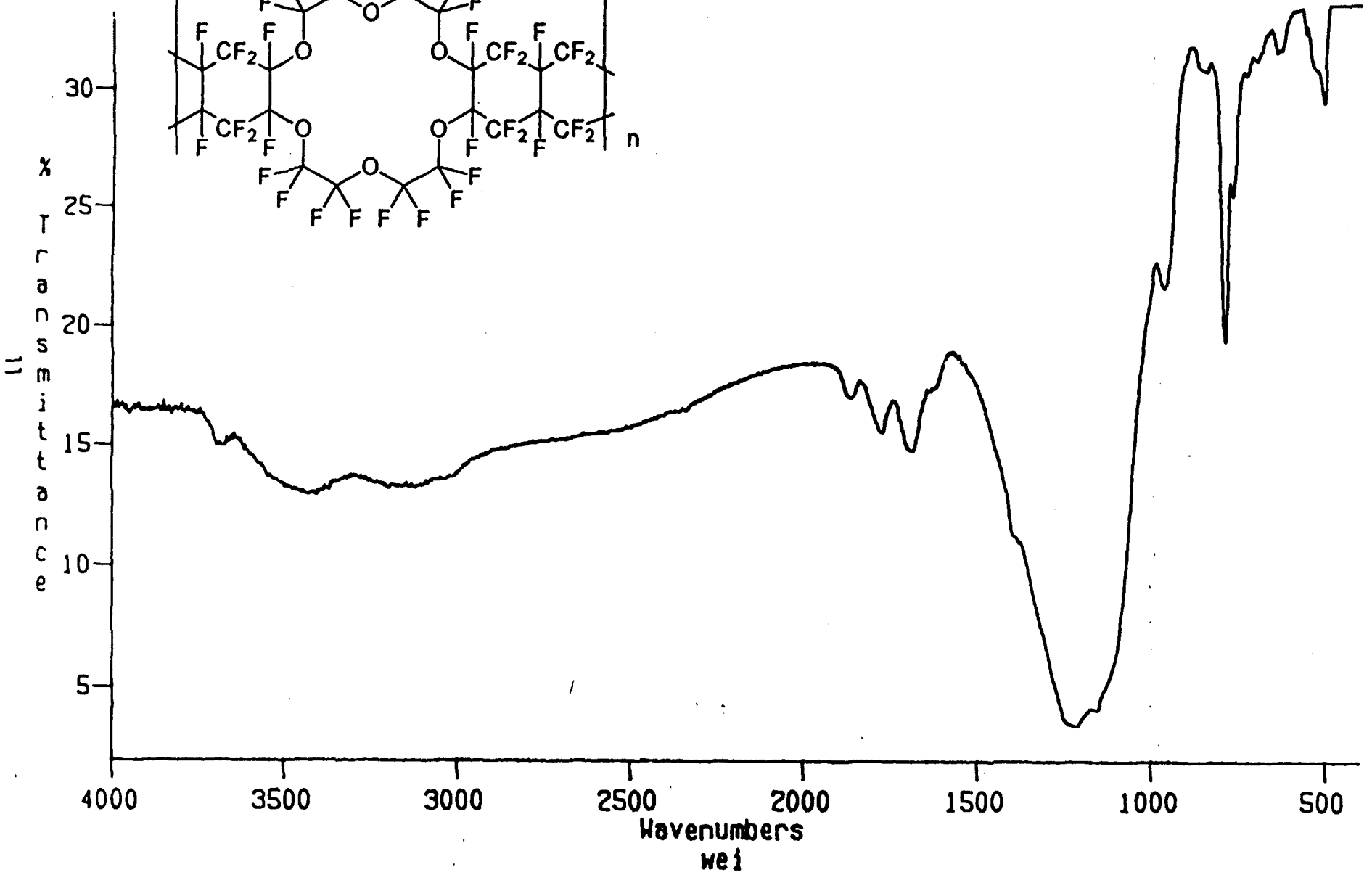
+/- C.I. Fragment	m/e
P - F	1393
P - C_6F_{11}	1131
P - OC_6F_{11}	1115

Mr. Han-Chao Wei of our research program has fluorinated this interesting crown ether polymer. We are very interested in exploring the defluorination process to see if we obtain the defluorinated material as indicated in the proposed structure.



He(cm^3/min.)	F_2(cm^3/min.)	Time(hr.)
50	0	0.5
50	2	24
25	2	24
10	3	24
3	3	24
0	3	24
25	0	0.5


30
25
20
15
10
5
0
% Transmittance
4000
3500
3000
2500
2000
1500
1000
Wavenumbers
wei
O
O
O
O
O
O
CH2
CH2
n


% Transmittance
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
wei
n

Elemental analyses of the Perfluoro-crown ether-polymer

	Found	Calculated
Carbon —	24.38% 24.34%	24.92%
Fluorine —	64.68% 64.59%	65.11%
Oxygen —	-----	9.97%

*Elemental analyses were done by **Schwarzkopf Microanalytical Laboratory** in New York